Problem 1: Proton – antiproton atom

We can use the expression for hydrogen-like atoms to calculate the energy levels.

\[ E_n = -\frac{2\pi Z^2 e^4 \mu}{(4\pi\varepsilon_0)^2 \hbar^2 n^2} \]

where \( Z \) is the total number of charges in the nucleus (\( = 1 \)), \( e \) is the electron charge (\( = 1.6022 \times 10^{-19} \) C), \( \mu \) is the reduced mass of the system with \( \mu = (m_1^{-1} + m_2^{-1})^{-1} \) and \( m_1 = m_2 = m_p = 1.6726 \times 10^{-27} \) kg, thus \( \mu = \frac{1}{2} m_p \), \( \varepsilon_0 \) is the permittivity of vacuum (\( = 8.8542 \times 10^{-12} \) C\(^2\) J\(^{-1}\) m\(^{-1}\)) [note: \( (4\pi\varepsilon_0)^{-1} \) is Coulomb's constant], \( \hbar \) is the Planck constant (\( = 6.626076 \times 10^{-34} \) J s) and \( n \) is the principal quantum number of the system taking values 1, 2, ...

For \( n = 1 \), \( E_1 = -\frac{m_p \left( \frac{e^2}{4\hbar \varepsilon_0} \right)^2}{2} = -2.00129 \times 10^{-13} \) J and for \( n = 2 \), \( E_2 = \frac{E_1}{4} \), hence

\[ \Delta E = E_2 - E_1 = 3 \frac{1}{4} E_1 = 1.50097 \times 10^{-15} \] J

\[ \Delta E = \frac{h \nu}{\hbar}, \text{hence } \nu = \frac{\Delta E}{\hbar} = \frac{1.50097 \times 10^{-15} \text{ J}}{6.626076 \times 10^{-34} \text{ J s}} = 2.2652 \text{ s}^{-1}. \]

\[ c = \lambda \nu, \text{ hence } \lambda = \frac{c}{\nu} = \frac{2.997925 \times 10^8 \text{ m s}^{-1}}{2.2652 \text{ s}^{-1}} = 1.3234 \times 10^{-10} \text{ m} = 1.3234 \text{ Å}. \]

The Bohr radius is given by

\[ \alpha = \frac{h^2 (4\pi \varepsilon_0)}{4\pi^2 \mu e^2} = \frac{2\hbar^2 \varepsilon_0}{m_p e^2} = 5.76397 \times 10^{-14} \text{ m which is } 1836/2 \text{ times smaller than the hydrogen radius due to the difference in reduced mass of the "atom".} \]

Problem 2: Annulene

The number of \( \pi \) electrons is 18. Two electrons can occupy each state due to the Pauli exclusion principle. Each state above the lowest is two-fold degenerate. Based on these pieces of information, we can fill this table:

<table>
<thead>
<tr>
<th>( N )</th>
<th>max number of ( e' ) per state</th>
<th>total ( e' ) up to this state</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>14</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>18</td>
</tr>
</tbody>
</table>

States up to \( N = 4 \) are fully occupied with 18 electrons. The lowest possible transition is from state \( N = 4 \) to state \( N = 5 \). The path forming a circular well is \( L = 18 \times 1.4 \text{ Å} \).

Hence

\[ \Delta E = E_5 - E_4 = (5^2 - 4^2) \left( \frac{6.6260755 \times 10^{-34} \text{ J s}}{2 \times (18 \times 1.4 \text{ Å})^2 \times 9.109389 \times 10^{-31} \text{ kg}} \right) = 3.415 \times 10^{-19} \text{ J} \]

The transition frequency is \( \nu = \Delta E/\hbar = 5.1544 \times 10^{14} \text{ s}^{-1} \) and the corresponding wavelength is \( \lambda = c/\nu = 581.6 \text{ nm} \).

Problem 3: Chemical bonding: The molecular ion \( O_2^{2+} \)

1. 171.9 kcal/mol
2. No
3. Yes
4. 85.6 kcal/mol
5. (171.9 − 85.6) kcal/mol = 86.3 kcal/mol or (86.3/N_A) kcal/molecule = 1.43 x 10^{-23} kcal/molecule.
6. ∼ 1.1 Å
7. ∼ 1.6 Å

**Problem 4: Electrochemistry: Nicad batteries**

\[ 2\text{NiO(OH)}(s) + 2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{Ni(OH)}_2(s) + 2\text{OH}^- \quad E_c^0 = -0.490 \text{ V} \]

\[ E_a = E_a^0 - \frac{RT}{2F} \ln \left[ \frac{\text{OH}^-}{2} \right]^2 \]

Cd (s) + 2OH^- \rightarrow Cd(OH)_2(s) + 2e^-

\[ E_a^0 = +0.809 \text{ V} \]

Cd (s) + 2NiO(OH) (s) + 2H_2O \xrightarrow{\text{charge}} 2Ni(OH)_2 (s) + Cd(OH)_2 (s)

\[ E = E_a - E_c = E_a^0 - E_c^0 = 0.809 \text{ V} - (-0.490 \text{ V}) = 1.299 \text{ V} \]

700 mAh = 0.700 A x 3600 s = 2520.0 C

2520.0 C → \frac{2520.0}{2.96485} \text{ moles of Cd = 0.013 moles of Cd → 0.013 x 112.4 = 1.47 g of Cd.}

**Problem 5: Boiler**

Tank capacity: \( m = V \rho = 4 \text{ m}^3 \times 0.73 \text{ g cm}^{-3} = 2920 \text{ kg} \)

Heating power \( P = 116 \text{ kW} \)

Consumption rate \( \frac{m}{t} = \frac{P}{\Delta h/m} = \frac{116 \text{ kJ s}^{-1}}{4.3 \times 10^7 \text{ J kg}^{-1}} = 2.70 \times 10^3 \text{ kg s}^{-1} (= 9.73 \text{ kg h}^{-1}) \)

Operation duration \( t = \frac{m}{P} = \frac{2920 \text{ kg}}{2.70 \times 10^3 \text{ kg s}^{-1}} = 1.08 \times 10^3 \text{ s} = 300 \text{ h} = 12.5 \text{ days} \)

\( \text{C}_n\text{H}_{2n+2} + \frac{1}{2}(3n+1) \text{O}_2 \rightarrow n\text{CO}_2 + (n+1)\text{H}_2\text{O} \)

\[
\frac{m_{\text{CO}_2}}{m_{\text{C}_n\text{H}_{2n+2}}} = \frac{44n}{14n+2} = \frac{22}{7 + \frac{1}{n}} \]

This ratio does not depend heavily on \( n \); for a representative value of \( n = 10 \), the ratio takes the value of 3.1.

Since \( \frac{m_{\text{C}_n\text{H}_{2n+2}}}{t} = 9.73 \text{ kg h}^{-1} \),

\[
\frac{m_{\text{CO}_2}}{t} = \frac{m_{\text{C}_n\text{H}_{2n+2}}}{m_{\text{CO}_2}} = 9.73 \text{ kg h}^{-1} \times 3.1 = 30.2 \text{ kg h}^{-1}
\]

**Problem 6: Ammonium nitrate**

Mixing is endothermic and the process is adiabatic, thus heat has to be provided by the solution itself. Since water is at its freezing point, it will tend to freeze, but the solution created will experience a depression of freezing point due to the presence of
dissolved ions. The large amount of heat required for solvation will necessitate some freezing of water.
A Hess cycle of 3 steps will be considered.
A. mixing at 0 °C with \( \Delta H_1 > 0 \)
B. lowering of the temperature of the mixture to its final temperature with \( \Delta H_2 < 0 \)
C. freezing of some water \( m_s \) with \( \Delta H_3 < 0 \)

The final temperature is given by \( \theta_2 = -K_f \frac{n}{m - m_s} \), where \( K_f \) is the cryoscopy constant, \( 2 \) is the number of particles per formula weight for \( \text{NH}_4\text{NO}_3 \), \( n \) the number of moles of \( \text{NH}_4\text{NO}_3 \), \( n = \frac{80 \text{ g}}{80 \text{ g mol}^{-1}} = 1 \text{ mol} \), \( m = 1000 \text{ g} \).

\( \Delta H_1 = \Delta h_n \times 1 \text{ mol} = -25.69 \text{ kJ} \)

\( \Delta H_2 = c_p \frac{m}{M} \theta_2 \), where \( c_p \) is the molar heat capacity of water and \( M \) its molecular mass (18 g mol\(^{-1}\)).

\( \Delta H_3 = -\Delta h_f \frac{m_s}{M} \), where \( \Delta h_f \) is the molar enthalpy of fusion.

\( \Delta H_1 + \Delta H_2 + \Delta H_3 = \Delta H_{\text{total}} = 0 \) because no heat is allowed to be exchanged between the system and its surroundings.

Substituting for \( \theta_2 \) and solving for \( m_s \) yields the following expression

\[
m_s = m - \frac{\Delta h_n nM}{\Delta h_f} \pm \sqrt{\left( \frac{m - \Delta h_n nM}{\Delta h_f} \right)^2 + \frac{2nK_f c_p m}{\Delta h_f}}
\]

We discount the solution derived from the + sign as unphysical (\( m_s > m \)) and arrive at the result \( m_s = 28.52 \text{ g ice} \).

Hence \( \theta_2 = -3.83 \text{ °C} \).

If we made the simplification that we expect \( m_s \ll m \), then \( \theta_2 \) is immediately calculated as \(-3.72 \text{ °C} \), which yields a value for \( m_s = 29.9 \text{ g} \). If this result is used to improve the \( \theta_2 \) value using the exact expression, we get \( \theta_2 = -3.83 \text{ °C} \). Then, \( m_s \) can be further improved to 28.5 g.

The process is spontaneous, irreversible, one where separation of components is possible, adiabatic, isobaric, isenthalpic, nearly isoenergetic.

The equation \( \Delta G = \Delta H - T \Delta S \) can be used here because \( T \) varies less than 2%. \( \Delta G < 0 \) because the process is spontaneous and \( \Delta H = 0 \), hence \( \Delta S > 0 \). This is also to be expected from stability criteria under the constraint \( \Delta H = 0 \).

**Problem 7: Carbon dioxide**

A qualitative one can be drawn based on the triple and the critical points. Since the room temperature is well above the triple point, there is no way there can be any solid CO$_2$ in the fire extinguisher. At 298 K, the CO$_2$ vapor pressure is 63.1 bar. This value can be estimated by drawing a straight line between the triple and the critical points. It can be calculated also based on the empirical Antoine equation, viz.,

\[
\log \frac{P}{\text{kPa}} = A - \frac{B}{C + \frac{T}{K}}
\]

with \(A = 6.46212, B = 748.28\) and \(C = -16.9\).

**Problem 8: Iron crystal**

(a) Let \(R\) be the atomic radius of iron and \(a = 2.87\) Å the length of the unit cell edge. Then, as atoms touch each other along the body diagonal and from a Pythagorean theorem in the cube:

\[
a\sqrt{3} = 4R \Rightarrow R = \frac{(a\sqrt{3})}{4} \Rightarrow R = 1.24\ \text{Å}
\]

The Avogadro number \(N_A\) can be calculated from the density \(\rho\) formula. The latter is obtained by finding the number of atoms per unit cell, multiplying this number by the mass of one atom (mol of atoms (g/mol) \(\times\) \(N_A\) (atoms/mol)) and, eventually, dividing the result by the volume of the unit cell \(a^3\). Note that each bcc unit cell contains two whole spheres, that is 2 Fe atoms.

\[
\rho(\text{g/cm}^3) = \frac{2 \times (55.847 / N_A)g}{a^3(\text{cm}^3)} \Rightarrow \rho(\text{g/cm}^3) = \frac{2 \times 55.847}{7.86 \times (2.87 \times 10^{-8})^3} \Rightarrow \rho = 6.01 \times 10^{23}
\]

(b) By applying the Pythagorean theorem in the cube, one finds:

\[
a^2 + a^2 = (4R)^2 \Rightarrow a = 2R\sqrt{2} \Rightarrow R = \frac{a\sqrt{2}}{4} \Rightarrow R = 1.27\ \text{Å} \ (\text{slightly different from the value found above for bcc structure, because of the different packing, having an influence on the atomic radius or at least its estimation.)}
\]

As for the density, recalling that each fcc unit cell contains four whole spheres, that is 4 Fe atoms, once again one has:

\[
\rho(\text{g/cm}^3) = \frac{4 \times (55.847 / N_A)g}{a^3(\text{cm}^3)} =
\]
\[ \frac{4 \times 55.847 \text{g}}{6.023 \times 10^{23} \times (3.59 \times 10^{-8})^3 \text{cm}^3} = 8.02 \text{g/cm}^3 \]

The higher value of \( \gamma \)-Fe density, as compared with \( \alpha \)-Fe, points at the fact that the fcc structure is denser than bcc. fcc represents the, so called, cubic close packed structure which, together with the hexagonal close packed, are the most efficient ways of packing together equal sized spheres in three dimensions. (c) and (d) The unit cells below are illustrated by using reduced size spheres. Note that, in hard spheres packing model the represented atoms must be in contact one to each other.

![Diagram of \( \alpha \)-Fe and \( \gamma \)-Fe unit cells]

According to the left figure, a perfectly fitted interstitial atom centered at \((\frac{1}{2}, 0, \frac{1}{2})\) in an \( \alpha \)-Fe cell, would have a radius of:

\[ R_{\text{interstitial}} = \frac{1}{2} a - R_{\text{Fe}} \]

where \( a = 2.87 \text{Å} \) and \( R_{\text{Fe}} = 1.24 \text{Å} \) [(see question (a)]. Therefore: \( R_{\text{interstitial}} \) (\( \alpha \)-Fe) = 0.20 Å

Similarly, according to the figure in right, a perfectly fitted interstitial atom centered at \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\) in an \( \gamma \)-Fe cell, would have a radius of:

\[ R_{\text{interstitial}} = \frac{1}{2} a - R_{\text{Fe}} \]

where \( a = 3.59 \text{Å} \) and \( R_{\text{Fe}} = 1.27 \text{Å} \) [(see question (b)]. Therefore: \( R_{\text{interstitial}} \) (\( \gamma \)-Fe) = 0.53 Å

(e) 1 nm = 10 Å. Thus:

For \( \alpha \)-Fe:

\[ \frac{R_{\text{carbon}}}{R_{\text{int interstitial}}} = \frac{0.77 \text{Å}}{0.20 \text{Å}} = 3.85 \]

For \( \gamma \)-Fe:

\[ \frac{R_{\text{carbon}}}{R_{\text{int interstitial}}} = \frac{0.77 \text{Å}}{0.53 \text{Å}} = 1.45 \]

Therefore, the carbon atom is roughly four times too large to fit next to the nearest iron atoms in \( \alpha \)-Fe without strain, while it is only 1.5 times oversize to fit in the \( \gamma \)-Fe structure. The above estimations explain well the low solubility of carbon in \( \alpha \)-Fe (< 0.1 %).

(f) The wavelength (\( \lambda \)) of the X-rays will be calculated from Bragg's law, assuming first order diffraction: \(2d \sin \theta = \lambda \), where \( \theta \) is the angle of diffraction equal to 32.6° and \( d \) is the interplanar spacing of the (200) set of parallel lattice planes, that is, the perpendicular distance between any pair of adjacent planes in the set. The (200) planes are shown
shaded in the figure.
Let $a$ be the length of the cubic unit cell edge. Then, from previous data for $\alpha$-Fe: $a = 2.87 \, \text{Å}$, so the distance between adjacent (200) planes is: $d = \frac{a}{2} = 1.44 \, \text{Å}$ Therefore, from Bragg's law: $\lambda = 2d \sin \theta = 2 \times 1.44 \times \sin(32.6^\circ) \Rightarrow \lambda = 1.55 \, \text{Å}$ This value corresponds to the $K_{\alpha 1}$ transition of iron.

**Problem 9: Cyclodextrine**

a) $V = a \times c \cdot b = a \times b \times c \sin(\beta) = 7474 \, \text{Å}^3$, $V_m = 7474 \, \text{Å}^3 / 4 = 1868 \, \text{Å}^3$

b) $FW = 1535.4 \, \text{g mol}^{-1}$, $\rho = FW \times (\text{V} \times N_A)$, hence $\rho = 1.3646 \, \text{g cm}^{-3}$

**Problem 10: Infrared spectroscopy**

1. The number of vibrational modes is given by $3N-6$ for non-linear and $3N-5$ for linear molecules, where $N$ is the number of atoms in the molecule. Hence

   CO: 1, H$_2$O: 3, C$_6$H$_5$: 30, C$_{60}$: 174

   2. The fact that the molecules have a vibrational infra red absorption implies that the molecules have a permanent dipole moment, hence these diatomic molecules must be heteronuclear.

   For a simple harmonic oscillator-type diatomic molecule, the eigen frequency is given by the equation $v = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$, where $k$ is the force constant and $\mu$ the reduced mass of the molecule. In the absence of any further information, nothing can be said about the reduce masses or the force constants (though bond strength is not related to $k$, but more likely to bond dissociation energy). The eigen frequency is equal to the frequency of the absorbed photons because the vibrational energy is given by $E_v = (v+\frac{1}{2}) \, h \, v$ and the energy for the resonance transition is $\Delta E = E_{v=1} - E_{v=0} = h \, v$.

**Problem 11: Radioactivity and chemical reactivity**

1. $\gamma$-rays are a form of high energy electromagnetic radiation.

2. There are no stable (non-radioactive) isotopes beyond Bi.

3. There are numerous light isotopes that are radioactive.

4. Xe compounds such as XeF$_2$ are commercially available.

5. Cs is the element with the lowest ionization potential (3.89 eV).

**Problem 12: Carbon dating**

a) Let $N_0$ be the $^{14}$C/$^{12}$C ratio in living systems and $N$ the same ratio found in a sample coming from a system that died $t$ years ago. Then, the following relation between them is true: $N = N_0 e^{-\lambda t}$, where $\lambda (= \ln 2 / t_\lambda)$ the disintegration constant for $^{14}$C. The above equation becomes

   $$ t = \frac{-\ln \frac{N}{N_0}}{\lambda} = \frac{-t_\lambda \ln N}{\ln 2} = \frac{-5700 \frac{\ln 0.25}{\ln 2}}{11400 \frac{y}{y}} = 11400 \frac{y}{y} $$

b) The $\beta$ decay scheme is based on the nuclear reaction $n \rightarrow p + \beta + \bar{\nu}_e$, where $p$ is a proton and $\bar{\nu}_e$ an electron antineutrino. In the case of $^{14}$C we have

   $$ ^{14}\text{C} \rightarrow ^{14}\text{N} + \beta + \bar{\nu} $$

   hence C becomes a (common) $^{14}$N atom.

c) If an organic molecule contains $^{14}$C, the consequence of its disintegration can be grave for the structure of the molecule, causing great damage to the molecule in
the vicinity of the $^{14}$C atom. At least the chemical bond is ruptured since $^{14}$N is a chemically different atom than $^{14}$C. Free radicals may also be created.
d) The total carbon inside a human body of 75 Kg is 75 kg x 0.185 = 13.9 kg. The total radioactivity (R) is $R = 0.277 \text{ Bq} / \text{g} \times 13.9 \text{ kg} = 3850 \text{ Bq}$
The amount of $^{14}$C present is estimated from the total radioactivity as follow:

$$R = \frac{dN}{dt} = \lambda N$$

Then

$$N = \frac{A}{\lambda} = A \cdot \frac{t_{1/2}}{\ln 2} = 3850 \text{ Bq} \cdot \frac{5700 \text{ y} \cdot 60 \times 60 \cdot 24 \times 365.25 \text{ s}}{0.693 \text{ y}} = 1.00 \times 10^{15} \text{ atoms} = 1.66 \text{ nmol}$$

**Problem 13: Uranium**

a) alpha decay: $X(A,Z) \rightarrow X(A-4, Z-2) + ^{4}\text{He}^{2+}(2p+2n)$

$$\Delta A = -4, \Delta Z = -2$$

beta decay: $X(A,Z) \rightarrow X(A, Z+1) + \beta + \bar{\nu}_e$

$$\Delta A = 0, \Delta Z = +1$$

Since changes in the mass number ($\Delta A$) are due to the emission of alpha particles only, in each series we have:

$$\text{total alpha particles emitted} = \frac{\Delta A_{\text{total}}}{4}$$

Alpha emission also changes the atomic number ($Z$) ($\Delta Z = -2$), so the total decrease in $Z$ due to the total alpha particles emitted would be twice their total number. But $Z$ of the final (stable) element of the radioactive series is higher than the expected $Z$ based on alpha emission. This difference in $Z$ is due to the number of beta particle emitted. Thus

$^{238}\text{U} \rightarrow ^{206}\text{Pb}$

$$\alpha = \Delta A/4 = (238-206)/4 = 32/4 = 8, \beta = 2\alpha - \Delta Z = 18 - (92-82) = 6$$

$^{235}\text{U} \rightarrow ^{207}\text{Pb}$

$$\alpha = \Delta A/4 = (235-207)/4 = 28/4 = 7, \beta = 2\alpha - \Delta Z = 14 - (92-82) = 4$$

b) This occurs when an alpha decay ($\Delta Z = -2$) is followed by two successive beta decays ($\Delta Z = +2$).

c) For each radioisotope of uranium we can write

$^{235}\text{U} = ^{235}\text{N}_0 \exp(-\lambda_{235} t)$ and $^{238}\text{U} = ^{238}\text{N}_0 \exp(-\lambda_{238} t)$

where $N$ is the number of nuclei at time $t$, $N_0$ at time $t = 0$ and $\lambda = \ln 2 / t_{1/2} = 0.693 / t_{1/2}$ the disintegration constant.

At $t = 0$, $^{235}\text{N}_0 = ^{235}\text{N}_0$, then

$$\frac{\exp(-\lambda_{238} t)}{\exp(-\lambda_{235} t)} = \frac{^{235}\text{N}}{^{238}\text{N}} = \frac{99.3}{0.7} = 142$$

Thus

$$\lambda_{238} t - \lambda_{235} t = \ln 142 = 4.95$$

$$\lambda_{238} = 0.693/t_{1/2} = 0.693/4.5 \times 10^9 = 1.54 \times 10^{-10} \text{ y}^{-1}$$

$$\lambda_{235} = 0.693/t_{1/2} = 0.693/7.1 \times 10^8 = 9.76 \times 10^{-10} \text{ y}^{-1}$$

$$t = \frac{4.95}{(9.76 - 1.54) \times 10^{-10} \text{ y}^{-1}} = \frac{4.95 \times 10^{10} \text{ y}}{8.22} = 6.0 \times 10^9 \text{ y}$$

d) The energy released by the complete fission of $1g$ $^{235}$U is

$$E = (1/235) \times 6.022 \times 10^{23} \times 200 \text{ MeV} = 5.13 \times 10^{23} \text{ MeV}$$

and the energy released upon combustion of $1g$ C is

$$E = (1/12) \times 6.022 \times 10^{23} \times 4.1 \text{ eV} = 2.06 \times 10^{23} \text{ eV} = 2.06 \times 10^{17} \text{ MeV}$$

Hence the amount of carbon that would release the same amount of energy as the fission of $1g$ $^{235}$U is

$$m = (5.13 \times 10^{23})/(2.06 \times 10^{17}) = 2.49 \times 10^3 \text{ kg C}$$
Problem 14: Lead iodide

1. The graph obtained is one of two straight lines, meeting at a peak of about 2.50 g Pb(NO₃)₂.

Data according to the reaction
2 KI(aq) + Pb(NO₃)₂(aq) → 2 KNO₃(aq) + PbI₂(s)

<table>
<thead>
<tr>
<th>Mass of Pb(NO₃)₂ (g)</th>
<th>Mass of PbI₂ (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.500</td>
<td>0.696</td>
</tr>
<tr>
<td>1.000</td>
<td>1.392</td>
</tr>
<tr>
<td>1.500</td>
<td>2.088</td>
</tr>
<tr>
<td>4.000 (1.000 g KI)</td>
<td>1.389</td>
</tr>
<tr>
<td>3.000 (2.000 g KI)</td>
<td>2.778</td>
</tr>
</tbody>
</table>

2. The total quantity of reactant is limited to 5.000 g. If either reactant is in excess, the amount in excess will be "wasted", because it cannot be used to form product. Thus, we obtain the maximum amount of product when neither reactant is in excess; there is a stoichiometric amount of each.

The balanced chemical equation for this reaction,
2 KI(aq) + Pb(NO₃)₂(aq) → 2 KNO₃(aq) + PbI₂(s)
shows that stoichiometric quantities are two moles of KI (166.00 g/mol) for each mole of Pb(NO₃)₂ (331.21 g/mol). If we have 5.000 g total, we can let the mass of KI equal \( x \) g, so that the mass of Pb(NO₃)₂ = (5.000 - \( x \)) g. Then we have

\[
\text{amount KI} = \frac{x \text{ g KI}}{166.00 \text{ g KI}} = \frac{x}{166.00}
\]

\[
\text{amount Pb(NO₃)₂} = \frac{(5.000 - x) \text{ g Pb(NO₃)₂}}{331.21 \text{ g Pb(NO₃)₂}} = \frac{5.000 - x}{331.21}
\]

At the point of stoichiometric balance, amount KI = 2 × amount Pb(NO₃)₂

\[
\frac{x}{166.00} = 2 \times \frac{5.000 - x}{331.21} \quad \text{or} \quad 331.21x = 10.00 \times 166.00 - 332.00x
\]

\[
x = \frac{1660.0}{331.21 + 332.00} = 2.503 \text{ g KI} \times \frac{1 \text{ mol KI}}{166.00 \text{ g KI}} = 0.01508 \text{ mol KI}
\]

\[
5.000 - x = 2.497 \text{ g Pb(NO₃)₂} \times \frac{1 \text{ mol Pb(NO₃)₂}}{331.21 \text{ g Pb(NO₃)₂}} = 0.007539 \text{ mol Pb(NO₃)₂}
\]

To determine the proportions precisely, we use the balanced chemical equation.
maximum PbI$_2$ mass = 2.503 g KI \times \frac{1 \text{ mol KI}}{166.00 \text{ g KI}} \times \frac{1 \text{ mol PbI}_2}{2 \text{ mol KI}} \times \frac{461.0 \text{ g PbI}_2}{1 \text{ mol PbI}_2} = 3.476 \text{ g PbI}_2

**Problem 15: Octahedral complexes**

d$^1$: t$^1_e g^0$
d$^2$: t$^2_e g^0$
d$^3$: t$^3_e g^0$
d$^4$: t$^4_e g^0$ (Δ > P) or t$^3_e g^1$ (Δ < P)
d$^5$: t$^5_e g^0$ (Δ > P) or t$^4_e g^2$ (Δ < P)
d$^6$: t$^6_e g^0$ (Δ > P) or t$^5_e g^2$ (Δ < P)
d$^7$: t$^6_e g^2$ (Δ > P) or t$^5_e g^2$ (Δ < P)
d$^8$: t$^6_e g^3$

**Problem 16: Isomerism in Inorganic Chemistry**

1. 27Co $[1s^22s^22p^63s^23p^6]$ 3d$^7$4s$^2$
   Ar
   Co$^{3+}$ [Ar]3d$^6$
   \[ \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \]  \[ \uparrow \downarrow \]  \[ \uparrow \uparrow \]  \[ \uparrow \uparrow \]  \[ \uparrow \downarrow \]  \[ \uparrow \downarrow \]

   2. dative covalent by the ligand into an empty metal orbital. d$^2$sp$^3$ hybridization

   \[ \uparrow \downarrow \uparrow \uparrow \uparrow \uparrow \]  \[ \uparrow \downarrow \]  \[ \uparrow \downarrow \uparrow \uparrow \uparrow \uparrow \]  \[ \uparrow \downarrow \]  \[ \uparrow \downarrow \uparrow \uparrow \uparrow \uparrow \]  \[ \uparrow \downarrow \]

   outer sphere paramagnetic complex

3. trans  cis

   4. \textit{fac}  \textit{mer}

   [Co(NH$_3$)$_5$Cl]Cl  \[ \text{A} \]

   [Co(NH$_3$)$_5$Cl$_2$]Cl  \[ \text{B} \]

5. 2 enantiomers $\pm$ Co(en)$_3$$^{3+}$
Problem 17: Tetrahedral and square complexes

3d
↑↓ | ↑↓ | ↑↓ | ↑↑ | ↑↑
sp²: tetrahedral/paramagnetic

4s
↑↓

4p
↑↓ | ↑↓ | ↑↓

dsp²: square planar/diamagnetic

Problem 18: Copper enzyme

1. Cu: 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰ 4s¹, Cu(I): 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁵,
   a. Cu(II): 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁹
2. Oxidised PC
3. A=\frac{e.c.l}{c} = 0.700 / (4500 \times 1) = 1.56 \times 10^{-4} \text{ mol dm}^{-3} \text{. 5 cm}^{3} \text{ of the solution contain 1.56} \times 10^{-4} \times 5 \times 10^{-3} \times 10500 \times 1000 = 8.2 \text{ mg PC.} \#\text{Cu atoms} = 1.56 \times 10^{-4} \times 5 \times 10^{-3} \times 6.0221 \times 10^{23} = 4.7 \times 10^{17}
4. Electronic configurations:
   Zn(II): 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰, Cd(II): 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰ 4s² 4p⁶ 4d¹⁰, Co(II): 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁷, Ni(II): 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁸. Redox inactive are the Zn(II) and Cd(II) reconstituted Blue Copper Proteins.

Problem 19: Palladium nanoclusters

1. \( N = \frac{N_s \cdot \rho \cdot V}{\text{Atomic Weight}} = 307 \text{ Pd(0) atoms per nanocluster} \)

\( V = \text{the volume of a nanocluster} = \frac{4}{3} \pi \left( \frac{D}{2} \right)^3 \)

According to the equation \( y=10r^2+2 \), the number of Pd(0) atoms in a 4 full-shells nanocluster is \( N = 1+12+42+92+162 = 309 \), hence it is a full shell cluster.

2. From Fig. 4 the H₂ uptake is \( \Delta P_{H_2} = 4.15 - 2.05 = 2.10 \text{ atm in 184 min.} \)

\( \Delta P_{H_2} V = \Delta n_{H_2} RT \), hence \( \Delta n_{H_2} = 0.029 \text{ mol where} V = 400-55=345 \text{ cm}^3 \)

Initially \( n_{Pd_{H_2}} = \frac{V \rho}{M} = \frac{5 \text{ cm}^3 \times 0.81 \text{ g cm}^{-3}}{6(612.0107 + 121.00794) \text{ g mol}^{-1}} = 0.048 \text{ mol} \)

(i) Conversion = \( \frac{\text{reacted moles}}{\text{initial moles}} = \frac{0.029}{0.048} = 0.60 = 60\% \)

(ii) The catalytically active Pd(0) atoms are \( \frac{162}{309} = 0.524 = 52.4\% \) of the total Pd(0) amount. So: \( \text{TON} = \frac{n_{H_2}}{n_{Pd}} = \frac{0.029 \text{ mol}}{0.524 \times 50 \times 10^{-6} \text{ mol}} = 1106 \) and \( \text{TOF} = \frac{\text{TON}}{t} = \frac{1106}{184 \text{ min}} = 6.0 \text{ min}^{-1} \)

3. The spectral regions (δ / ppm) and the respective relative integrals in the ¹H-NMR spectrum of hex-1-ene (Fig. 5a and Table) are assigned as follows:

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃(CH₂)₂CH₂CH=CH₂</td>
<td>0.88-0.96</td>
<td>1.15-1.32</td>
<td>1.99-2.08</td>
<td>5.65-5.79</td>
</tr>
</tbody>
</table>
The integral ratios of the second $^1$H-NMR spectrum (Fig. 5b and Table) suggest that both hex-1-ene and hexane are present. The differences in the integral values of the spectral regions 0.88-0.96 ppm and 1.12-1.37 ppm must be due to the presence of hexane. The relative integrals of second spectrum are converted as shown in the table below:

<table>
<thead>
<tr>
<th>Solution of the reaction (Fig. 5b)</th>
<th>$\delta$ / ppm</th>
<th>relative integral</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.88-0.96</td>
<td>3+6</td>
<td></td>
</tr>
<tr>
<td>1.12-1.37</td>
<td>4+8</td>
<td></td>
</tr>
<tr>
<td>1.99-2.08</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>4.85-4.98</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>5.65-5.79</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

So, the spectral regions ($\delta$ / ppm) and the respective relative integrals in the $^1$H-NMR spectrum corresponding to hexane are assigned as follows:

<table>
<thead>
<tr>
<th>$1'$</th>
<th>$2'$</th>
<th>$1''$</th>
<th>$2''$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$(CH$_2$)$_2$CH$_3$</td>
<td>0.88-0.96</td>
<td>1.15-1.32</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(6)</td>
<td>(8)</td>
<td></td>
</tr>
</tbody>
</table>

Finally, comparing the integral values per proton for the hex-1-ene and hexane the % conversion of hex-1-ene to hexane, after 30 min is 50%.

**Problem 20: Drug kinetics**

$$A_a \xrightarrow{k_1} A_b \rightarrow \text{products} \quad (1)$$

$$-\frac{d[A]}{dt} = k_1[A]_a \quad (2)$$

Integration of Eq. 2 gives $[A]_t = [A]_0 \exp(-k_1t)$, where $[A]_0$ the concentration of the drug in the stomach at zero time.

![Graph showing the concentration of drug](image)

$$\frac{[A]_b - [A]_a}{[A]_a} = 0.75 \Rightarrow [A]_a = 0.25 = \left(\frac{1}{2}\right)^2$$

Since ¼ of the initial amount remains after one hour, $(\frac{1}{2})^2 = 1/16 = 0.625$ will remain after 2 hours, which corresponds to 4 half lives. That is 6.25% of $[A]_a$ is left.
Problem 21: \( \text{Br}_2 + \text{CH}_4 \) reaction mechanism

1 The rate of formation of \( \text{CH}_3\text{Br} \) is given by the equation:

\[
v = \frac{d[\text{CH}_3\text{Br}]}{dt} = k_3[\text{CH}_3][\text{Br}_2]\]

(1)

The “steady state” approximations for \( \text{CH}_3 \) and \( \text{Br} \) are given by the equations:

\[
\frac{d[\text{CH}_3]}{dt} = k_2[\text{Br}][\text{CH}_4] - [\text{CH}_3][k_3[\text{Br}_2] + k_4[\text{HBr}]] = 0
\]

(2)

\[
\frac{d[\text{Br}]}{dt} = 2k_1[\text{Br}_2][\text{M}] - k_2[\text{Br}][\text{CH}_4] + [\text{CH}_3][k_3[\text{Br}_2] + k_4[\text{HBr}]] - 2k_5[\text{Br}][\text{M}] = 0
\]

(3)

From equation (2):

\[
[\text{CH}_3] = \frac{k_2[\text{Br}][\text{CH}_4]}{k_3[\text{Br}_2] + k_4[\text{HBr}]}
\]

(4)

From equations (3) and (4):

\[
[\text{Br}] = \left(\frac{k_1}{k_5}\right)^{\frac{1}{2}}[\text{Br}_2]^{\frac{1}{2}}[\text{HBr}]^{\frac{1}{2}}
\]

(5)

By combining equations (1), (4) and (5) the expression for the rate of formation of \( \text{CH}_3\text{Br} \) as a function of the concentrations of the stable species that are involved in the reaction is given by equation (6):

\[
v = \left(\frac{k_1}{k_5}\right)^{\frac{1}{2}}k_2\frac{[\text{Br}_2]^{\frac{1}{2}}[\text{CH}_4]}{k_3[\text{Br}_2] + 1}
\]

(6)

2

<table>
<thead>
<tr>
<th>Start of the reaction</th>
<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steady state condition</td>
<td>I</td>
</tr>
<tr>
<td>Near to the end of the reaction</td>
<td>III</td>
</tr>
</tbody>
</table>

3

| Start of the reaction | [\text{Br}_2] >> [\text{HBr}] and since \( k_3 = k_4 \):
|-----------------------| \( k_3[\text{Br}_2] >> k_4[\text{HBr}] \), so \( \frac{k_4[\text{HBr}]}{k_3[\text{Br}_2]} << 1 \) |
| Steady state condition | - |
| Near to the end of the reaction | [\text{Br}_2] << [\text{HBr}] and since \( k_3 = k_4 \):
|-----------------------| \( k_3[\text{Br}_2] << k_4[\text{HBr}] \), so \( \frac{k_4[\text{HBr}]}{k_3[\text{Br}_2]} >> 1 \) |
Problem 22: Buffer solutions

1. The equilibrium, which governs the concentration of $H^+$ within the solution is

$$\text{HCOOH} \leftrightarrow \text{HCOO}^- + H^+$$

Hence $K_s = \frac{[H^+][\text{HCOO}^-]}{[\text{HCOOH}]} = 2.1 \times 10^{-4}$

and since $[\text{HCOOH}] = 0.200 \text{ M}$ and $[\text{HCOO}^-] = 0.150 \text{ M}$

$$[H^+] = 2.1 \times 10^{-4} \times \frac{0.200}{0.150} = 2.8 \times 10^{-4} \text{ M}$$

and $\text{pH} = 3.55$.

2. Since sodium hydroxide reacts with formic acid:

$$\text{HCOOH} + \text{OH}^- \rightarrow \text{HCOO}^- + \text{H}_2\text{O}$$

the concentration of formic acid in the solution is reduced to

$[\text{HCOOH}] = 0.200 \text{ M} - 0.0100 \text{ M} = 0.190 \text{ M}$

and the concentration of formate is increased to

$[\text{HCOO}^-] = 0.150 \text{ M} + 0.0100 \text{ M} = 0.160 \text{ M}$

Therefore:

$$[H^+] = 2.1 \times 10^{-4} \times \frac{0.190}{0.160} = 2.5 \times 10^{-4} \text{ M}$$

and $\text{pH} = 3.60$

Note that the addition of sodium hydroxide, which is a strong base, causes a very small increase of the pH of the solution.

3. Let V the volume of the solution of sodium hydroxide. Therefore, the final volume of the solution will be $(100.0 + V) \text{ mL}$ and the number of mmol of CH$_3$COOH and OH$^-$ which are mixed are $100.0 \text{ mL} \times 0.150 \text{ mmol/mL} = 15.00 \text{ mmol}$ and $V \text{ mL} \times 0.200 \text{ mmol/mL} = 0.200 \times V \text{ mmol}$, respectively. From the reaction:

$$\text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O}$$

it is obvious that the amount of acetate produced is $0.200 \times V \text{ mmol}$ and the amount of acetic acid which remains unreacted is $(15.00 - 0.200 \times V) \text{ mmol}$. Hence, the concentration of each constituent in the buffer solution is:

$$[\text{CH}_3\text{COOH}] = \frac{(15.00 - 0.200 \times V)}{100.0 + V} \text{ M}$$

and $[\text{CH}_3\text{COO}^-] = \frac{0.200 \times V}{100.0 + V} \text{ M}$

From the acid dissociation constant expression of acetic acid

$$K_s = \frac{[\text{CH}_3\text{COO}^-][H^+]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5}$$

it can be derived

$$\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{K_s}{[H^+]^2} = \frac{1.8 \times 10^{-5}}{2.5 \times 10^{-4}} = 0.72$$

and

$$\frac{0.200 \times V}{100.0 + V} \text{ M} \times \frac{1.0 \times 10^{-5}}{0.200 \times V} \text{ M} = 1.8 \times 10^{-5}$$

from which $V = 48.21 \text{ cm}^3$.

4. a

5. (i) c, (ii) b

6. (i) b, (ii) d

7. (i) c, (ii) c
Problem 23: Titrations of weak acids

The titration reaction is
\[ \text{CH}_3\text{COOH} + \text{OH}^- \leftrightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \]
a) Initial pH

The pH of the solution before the titration begins, is calculated by the acid dissociation constant and the initial concentration of CH₃COOH:
\[ \text{CH}_3\text{COOH} \leftrightarrow \text{CH}_3\text{COO}^- + \text{H}^+ \]
From the acid dissociation constant expression:
\[ K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5} \]
the concentration of H⁺ can be calculated:
\[ [\text{H}^+] = \sqrt{1.8 \times 10^{-5} \times 0.1000} = 1.34 \times 10^{-3} \text{ M and pH} = 2.87 \]
b) pH after the addition of 10.00 cm³ of titrant

The solution contains acetic acid and sodium acetate. Therefore it is a buffer solution. The concentration of each constituent is calculated:
\[ [\text{CH}_3\text{COOH}] = \frac{(50.00 \text{ cm}^3 \times 0.1000 \text{ M}) - (10.00 \text{ cm}^3 \times 0.1000 \text{ M})}{60.00 \text{ cm}^3} = 0.0667 \text{ M} \]
\[ [\text{CH}_3\text{COO}^-] = \frac{10.00 \text{ cm}^3 \times 0.1000 \text{ M}}{60.00 \text{ cm}^3} = 0.01667 \text{ M} \]

These concentrations are then substituted into the dissociation constant expression of acetic acid for calculating the concentration of [H⁺]:
\[ [\text{H}^+] = 1.8 \times 10^{-5} \times \frac{0.0667}{0.01667} = 7.20 \times 10^{-5} \text{ M and pH} = 4.14 \]
c) pH at the equivalence point

At the equivalence point, all acetic acid has been converted to sodium acetate and the pH is calculated from the hydrolysis of acetate ions:
\[ \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \leftrightarrow \text{CH}_3\text{COOH} + \text{OH}^- \]
The volume of titrant required for the equivalence point (Vₑp) is calculated:
\[ Vₑp = \frac{50.00 \text{ cm}^3 \times 0.1000 \text{ M}}{0.1000 \text{ M}} = 50.00 \text{ cm}^3 \]

and the total volume of solution is 100.0 cm³. Therefore, at this point of the titration
\[ [\text{CH}_3\text{COOH}] = [\text{OH}^-] \text{ and } \]
\[ [\text{CH}_3\text{COO}^-] = \frac{50.00 \text{ cm}^3 \times 0.1000 \text{ M}}{100.0 \text{ cm}^3} - [\text{OH}^-] = 0.0500 \text{ M} \]
\[ \frac{[\text{OH}^-]^2}{0.0500 \text{ M}} = \frac{\text{K}_w}{\text{K}_a} = \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10} \]
\[ [\text{OH}^-] = \sqrt{0.0500 \times 5.56 \times 10^{-10}} = 5.27 \times 10^{-6} \text{ M} \]
pOH = 5.28 and thus pH = 14-5.28 = 8.72
d) pH after the addition of 50.10 cm³ of titrant

At this stage, all acetic acid has been converted to sodium acetate and the pH of the solution is calculated by the excess of sodium hydroxide, which has been added:
\[ [\text{OH}^-] = \frac{(50.10 \text{ cm}^3 \times 0.1000 \text{ M}) - (50.00 \text{ cm}^3 \times 0.1000 \text{ M})}{100.1 \text{ cm}^3} = 1.0 \times 10^{-4} \text{ M} \]
Therefore pOH = 4.00 and pH = 10.00
e) Selection of indicator
Since the pH at the equivalence point is 8.72, the appropriate acid base indicator is phenolphthalein.

2. (i) b, (ii) c, (iii) a, (iv) b, (v) c, (vi) d

Problem 24: Separation by extraction

1 Starting with an amount \( W_0 \) of S in phase 1, after the extraction this amount is distributed between the two phases as follows:
\[ W_0 = (C_S)_1 V_1 + (C_S)_2 V_2 \]
Since \( D = (C_S)_2 / (C_S)_1 \), we have
\[ W_0 = (C_S)_1 V_1 + D(C_S)_1 V_2 = (D V_2 + V_1)(C_S)_1 \]
Therefore, after removing phase 2, the remaining amount of S in phase 1 is:
\[ W_1 = (C_S)_1 V_1 = \frac{V_1}{D V_2 + V_1} W_0 \]

By repeating extraction with a fresh portion of volume \( V_2 \) of phase 2, the amount \( W_1 \) of S is similarly distributed. After removing phase 2, the remaining amount of S in phase 1 is:
\[ W_2 = (C_S)_1 V_1 = \frac{V_1}{D V_2 + V_1} W_1 = \frac{V_1}{D V_2 + V_1} \left( \frac{V_1}{D V_2 + V_1} \right)^2 \]

and so on. Therefore after \( n \) extractions with a fresh portion of volume \( V_2 \) of phase 2, the remaining amount of S in phase 1 will be:
\[ W_n = W_0 \left( \frac{V_1}{D V_2 + V_1} \right)^n \]

2. (a) The remaining fraction of S after 1 extraction with 100 mL of chloroform is calculated using Equation 1.4:
\[ f_1 = \frac{W_1}{W_0} = \frac{50}{3.2 \times 100 + 50} = 0.135, \]
therefore the percentage of S extracted is 100 - 13.5 = 86.5%

(b) The remaining fraction of S after 4 extractions with 25 mL of chloroform each time is similarly calculated:
\[ f_4 = \frac{W_4}{W_0} = \left( \frac{50}{3.2 \times 25 + 50} \right)^4 = 0.022, \]
therefore the percentage of S extracted is 100 - 2.2 = 97.8%. The result is indicative of the fact that successive extractions with smaller individual volumes of extractant are more efficient than a single extraction with all the volume of the extractant.

3. Using Equation 1-4 we have:

\[
0.01 = \left( \frac{100.0}{9.5 \times 25.0 + 100.0} \right)^n \text{ or } 0.01 = 0.2963^n \text{ hence } n = \log(0.01)/\log(0.2963) = 3.78, \text{ therefore at least 4 extractions are required.}
\]

4. The equilibria involved are represented schematically as follows:

\[
\begin{align*}
\text{HA} & \quad \overset{K_A}{\rightleftharpoons} \quad \text{H}^+ + \text{A}^- \\
\text{organic phase} & \quad \leftrightarrow \\
\text{aqueous phase}
\end{align*}
\]

We have (subscripts \(w\) and \(o\) denote concentrations in aqueous and organic phase, respectively)

\[
D = \frac{(C_{HA})_o}{(C_{HA})_w} = \frac{[HA]_o}{(HA)_w + [A^-]_w}
\]

\[
K_D = \frac{[HA]_o}{[HA]_w} \quad \text{and} \quad K_a = \frac{[H^+]_w [A^-]_w}{[HA]_w}
\]

Combining all three equations we finally obtain:

\[
D = \frac{K_D [H^+]_w}{[H^+]_w + K_a} \quad (1.5)
\]

Last equation predicts that if \([H^+]_w >> K_a\) (strongly acidic aqueous phase), then \(D = K_D\) (i.e. \(D\) acquires the maximum possible value) and the acid is extracted (or prefers to stay) in the organic phase. On the other hand, if \([H^+]_w << K_a\) (strongly alkaline aqueous phase), we have \(D = K_D[H^+]_w/K_a\), and because of the small value of \(D\) the acid is then extracted (or prefers to stay) in the aqueous phase. In this way, by regulating the pH of the aqueous phase, the course of extraction is shifted towards the desired direction.

5. (a) By using the previously derived Equation 1.5, we obtain the following plots of the \(D/K_D\) ratio vs. pH.

(b) From these plots it is clear that at the pH region 7-8 the distribution ratio for benzoic acid will be practically 0, whereas that of phenol will acquire the maximum possible value. Therefore, phenol can be efficiently separated from an aqueous solution of both compounds by extraction with diethylether, provided that the pH of this solution has been adjusted in the range 7 to 8 (e.g. by the presence of excess of NaHCO\(_3\)).
6. (a) The equilibria involved are represented schematically as follows:

\[ \text{organic phase} \]

\[ \text{aqueous phase} \]

\[ \text{OxH} \]

\[ \text{Ox}^- \]

\[ \text{K}_1 \hspace{1cm} \text{K}_2 \]

\[ \text{OxH} \hspace{1cm} \text{OxH}_2^+ \]

We have the expressions

\[ D = \frac{[\text{OxH}]_o}{[\text{OxH}]_w} \]

\[ K_D = \frac{[\text{OxH}]_o}{[\text{OxH}]_w} = 720 \]

\[ K_1 = \frac{[\text{OxH}]_w[H^+]_w}{[\text{OxH}_2^+]_w} = 1 \times 10^{-5} \]

\[ K_2 = \frac{[\text{Ox}^-]_w[H^+]_w}{[\text{OxH}]_w} = 2 \times 10^{-10} \]

Combining all four equations, we have the sought-for expression

\[ D = \frac{[\text{OxH}]_w}{K_1[H^+]_w + [\text{OxH}]_w + \frac{K_2 [\text{OxH}]_w}{[H^+]_w}} = \frac{K_D}{K_1[H^+]_w + 1 + \frac{K_2}{[H^+]_w}} \]

(b) Using last equation we obtain the following D-pH plot:

(c) We calculate the 1st and 2nd derivative of the denominator, i.e.,

\[ F([H^+]_w) = \frac{[H^+]_w}{K_1} + 1 + \frac{K_2}{[H^+]_w} \]

whereupon we have the 1st derivative \( F'([H^+]_w) = \frac{1}{[H^+]_w} - \frac{K_2}{[H^+]_w} \)

and for the 2nd derivative \( F''([H^+]_w) = \frac{2K_2}{[H^+]_w} \)
Since always $F''([H^+]_w) > 0$, then when $F'([H^+]_w) = 0$, $F([H^+]_w)$ is minimum under these conditions. Consequently, the distribution ratio is maximum when

$$\frac{1}{K_1} - \frac{K_2}{[H^+]^2} = 0$$

or $[H+]_w = \sqrt{K_1 K_2} = \sqrt{(1 \times 10^{-3})(2 \times 10^{-10})} = 4.5 \times 10^{-8}$ M

or pH = 7.35

**Problem 25: Mass Spectroscopy**

1. The ionic fragment SiCl$_2^+$ will be represented by the following peaks:

   - M = 98 $^{28}$Si$^{35}$Cl$_2^+$
   - M+1 = 99 $^{29}$Si$^{35}$Cl$_2^+$
   - M+2 = 100 $^{28}$Si$^{35}$Cl$^{37}$Cl$^+$ + $^{30}$Si$^{35}$Cl$_2^+$
   - M+3 = 101 $^{29}$Si$^{35}$Cl$^{37}$Cl$^+$
   - M+4 = 102 $^{30}$Si$^{35}$Cl$_2^+$ + $^{28}$Si$^{35}$Cl$^{37}$Cl$^+$
   - M+5 = 103 $^{29}$Si$^{37}$Cl$_2^+$
   - M+6 = 104 $^{30}$Si$^{37}$Cl$_2^+$

Therefore, the correct answer is 7.

2. The expected peaks and the corresponding probabilities are:

   - m/z = 45 $^{10}$B$^{35}$Cl : 0.199x0.7577 = 0.151
   - m/z = 46 $^{11}$B$^{35}$Cl : 0.801x0.7577 = 0.607
   - m/z = 47 $^{10}$B$^{37}$Cl : 0.199x0.2423 = 0.048
   - m/z = 48 $^{11}$B$^{37}$Cl : 0.801x0.2423 = 0.194

Hence, the base peak has nominal mass M = 46 and the relative intensities are:

   - M−1 = 45 (0.151/0.607)x100 = 24.9%
   - M = 46 = 100%
   - M+1 = 47 (0.048/0.607)x100 = 7.9%
   - M+2 = 48 (0.194/0.607)x100 = 32.0%

Therefore, the correct answer is C.

3. For the ion N$_2^+$ we have:

   - M: $^{14}$N$^{14}$N = (0.99634)$^2$ = 0.9927
   - M+1: $^{14}$N$^{15}$N + $^{15}$N$^{14}$N = 2x(0.99634x0.00366) = 0.007293

   hence, (M+1)/M = 0.007293/0.9927 = 0.00735 or 0.735%

For the ion CO$^+$ we have:

   - M: $^{12}$C$^{16}$O = 0.989x0.99762 = 0.9866
   - M+1: $^{12}$C$^{17}$O + $^{13}$C$^{16}$O = (0.989x0.00038) + (0.11x0.99762) = 0.01135

   hence, (M+1)/M = 0.01135/0.9866 = 0.0115 or 1.15%

For the ion CH$_2$N$^+$ we have:

   - M: $^{12}$C$^{1}$H$_2^{14}$N = 0.989x(0.99985)$^4$x0.99634 = 0.9851
   - M+1: $^{12}$C$^{1}$H$_2^{15}$N + $^{12}$C$^{1}$H$^2$H$^{14}$N + $^{12}$C$^{2}$H$^1$H$^{14}$N + $^{12}$C$^{1}$H$_2^{15}$N =
     0.011x(0.99985)$^4$x0.99634+2x0.989x0.99985x0.00015x0.99634 +
     0.989x(0.99985)$^5$x0.00366 = 0.01487

   hence, (M+1)/M = 0.01487/0.9851 = 0.0151 or 1.51%

For the ion C$_2$H$_4^+$ we have:

   - M: $^{12}$C$_2$H$_4$ = (0.989)$^2$x(0.99985)$^4$ = 0.9775
   - M+1: $^{13}$C$^{12}$C$^{1}$H$_4$ + $^{12}$C$^{13}$C$^{1}$H$_4$ + $^{12}$C$^{2}$C$^{2}$H$^2$H$^{1}$H$_3$ + $^{12}$C$_2$H$^2$H$^{2}$H$^2$H$_3$ +
     $^{12}$C$_2$H$_2^{1}$H$^2$H$^{1}$H$_3$ + $^{12}$C$_2$H$^2$H$^2$H$^2$H$_3$ = 2x0.011x0.989x(0.99985)$^4$ +
     4x0.989x0.00015x(0.99985)$^3$ = 0.02234

   hence, (M+1)/M = 0.02234/0.9775 = 0.0229 or 2.29%

Therefore the correct answer is (b) CO$^+$
Problem 26  Chemical Structure and Absolute Stereochemistry of Coniine

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{N} & \quad \text{1. CH}_3\text{I (Excess)} \\
\text{H} & \quad \text{2. Ag}_2\text{O, H}_2\text{O}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{N} & \quad \text{OH}^- \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{H} & \quad \Delta \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{N} & \quad \text{(CH}_3\text{)}_2
\end{align*}
\]

\[
\begin{align*}
\text{A} & \quad 1. \text{CH}_3\text{I} \\
\text{A} & \quad 2. \text{Ag}_2\text{O, H}_2\text{O}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{Me} & \quad \Delta \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{H} & \quad \Delta
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_3 & \quad \text{1,4-octadiene} \\
\text{CH}_3\text{CH}_2\text{CH}_3 & \quad \text{1,5-octadiene}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{N} & \quad \text{C}_6\text{H}_5\text{CH}_2\text{OCOCI (Z-Cl)} \\
\text{NaOH, 0°C} & \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{N} \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{H} & \quad \text{KMN}_4 \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{H} & \quad \text{ZHN} \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{H} & \quad \text{COOH}
\end{align*}
\]

\[
\begin{align*}
\text{H}_2, \text{Pd/C} & \quad \text{H}_2\text{N} \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{H} & \quad \text{COOH}
\end{align*}
\]

(S)-5-amino-octanoic acid

Problem 27: The chemistry and identification of flavonoids

1.

![Chemical Structure B](image)

2. a) down field. The $^1$H-NMR resonance of phenolic proton involvement in hydrogen bonding will be observed at very low magnetic field ($\sim 12$ppm).

3.

![Chemical Structure D](image)

4. $^{13}$C-NMR would be expected to show three characteristic peaks of the three different carbonyl groups.

![Chemical Structure C](image)
Problem 28: Synthesis of peptides

1

\[
\begin{align*}
\text{H}_2\text{N} & \text{CONH} \text{C}_6\text{H}_5 \text{CO}_2\text{H} \\
\text{H}_2\text{N} & \text{CONH} \text{C}_6\text{H}_5 \text{CO}_2\text{H} \\
\text{H}_2\text{N} & \text{CONH} \text{C}_6\text{H}_5 \text{CO}_2\text{H} \\
\text{H}_2\text{N} & \text{CONH} \text{C}_6\text{H}_5 \text{CO}_2\text{H}
\end{align*}
\]

Dipeptide I  
Dipeptide II  
Dipeptide III  
Dipeptide IV

The cyclic dipeptides (diketo piperazines) must also be considered:

\[
\begin{align*}
\text{HN} & \text{CONH} \\
\text{HN} & \text{CONH} \\
\text{HN} & \text{CONH}
\end{align*}
\]

DP-I  DP-II  DP-III

2. Best answers are 5 and 2.

3.

4. Benzyl chloroformate, reagent N° 4, would react easily with an amine in the following way:

\[
\text{C}_6\text{H}_5\text{CH}_2\text{OCOCl} + \text{H}_2\text{NR} \xrightarrow{\text{base}} \text{C}_6\text{H}_5\text{CH}_2\text{OCONHR} + \text{HCl}
\]

5. If we assume the intermediate formation of a carbonium ion, the ease of formation of such ion would parallel its stability. Electron delocalization is most extensive in case D:

And least effective in case A:

In the same way the cation from B is better stabilized than the cation from C. Therefore, the order of increasing lability is: A<B<C<D.
Problem 29: Oleuropein hydrolysis

1.

(a)

(b)

2.

3.

The correct structure is C
Problem 30: Stereochemistry of the Addition Reactions to Alkenes

a)  
\[
\begin{array}{c}
\text{Br} \quad \text{(R)} \\
\text{H} \\
\text{H} \\
\text{C} \quad \text{C} \\
\text{H} \\
\text{CH}_3 \\
\end{array}
\quad
\begin{array}{c}
\text{CH}_3 \\
\text{H} \\
\text{Br} \\
\text{H} \\
\text{Br} \\
\text{H} \\
\text{CH}_3 \\
\end{array}
\quad
\begin{array}{c}
\text{CH}_3 \\
\text{Br} \\
\text{H} \\
\text{Br} \\
\text{H} \\
\text{Br} \\
\text{CH}_3 \\
\end{array}
\quad
\text{No}
\quad
\text{Yes}
\]

b)  
\[
\begin{array}{c}
\text{H}_3\text{C} \quad \text{H} \\
\text{H} \\
\text{C} \quad \text{C} \quad \text{(S)} \quad \text{Br} \\
\text{H} \\
\text{H}_3\text{C} \\
\text{H} \\
\text{CH}_3 \\
\end{array}
\quad
\begin{array}{c}
\text{CH}_3 \\
\text{Br} \\
\text{Br} \\
\text{Br} \\
\text{H} \\
\text{CH}_3 \\
\end{array}
\quad
\begin{array}{c}
\text{CH}_3 \\
\text{H} \\
\text{Br} \\
\text{Br} \\
\text{Br} \\
\text{CH}_3 \\
\end{array}
\quad
\text{No}
\quad
\text{Yes}
\]

c)  
\[
\begin{array}{c}
\text{H}_3\text{C} \quad \text{(S)} \\
\text{Br} \\
\text{H} \\
\text{H}_3\text{C} \quad \text{(R)} \\
\text{C} \quad \text{C} \\
\text{H} \\
\text{H} \\
\text{CH}_3 \\
\end{array}
\quad
\begin{array}{c}
\text{CH}_3 \\
\text{Br} \\
\text{Br} \\
\text{Br} \\
\text{H} \\
\text{H} \\
\text{Br} \\
\text{CH}_3 \\
\end{array}
\quad
\begin{array}{c}
\text{CH}_3 \\
\text{Br} \\
\text{Br} \\
\text{Br} \\
\text{H} \\
\text{Br} \\
\text{CH}_3 \\
\end{array}
\quad
\text{Yes}
\quad
\text{Yes}
\]

d)  
\[
\begin{array}{c}
\text{H}_3\text{C} \quad \text{H} \\
\text{H} \\
\text{C} \quad \text{(S)} \quad \text{Br} \\
\text{H} \\
\text{H}_3\text{C} \\
\text{H} \\
\text{CH}_3 \\
\end{array}
\quad
\begin{array}{c}
\text{CH}_3 \\
\text{Br} \\
\text{Br} \\
\text{Br} \\
\text{H} \\
\text{H} \\
\text{Br} \\
\text{CH}_3 \\
\end{array}
\quad
\begin{array}{c}
\text{CH}_3 \\
\text{H} \\
\text{Br} \\
\text{Br} \\
\text{Br} \\
\text{H} \\
\text{Br} \\
\text{CH}_3 \\
\end{array}
\quad
\text{No}
\quad
\text{No}
\]

23
Problem 31: Identification of Organic Compounds

(A) \[ \text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH}_3 \] \[ \text{H}_2/\text{Pd/C} \] \[ \text{CH}_3 \]

(B) \[ \text{COOH} \]

(C) \[ \text{COOH} \text{OH} \]

Problem 32: Lipases

a)

\[ \text{C-CH}_3 \] \[ \text{C} \] \[ \text{C-CH}_2\text{Cl} \] \[ \text{C-CCl}_3 \] \[ \text{C-CF}_3 \] \[ \text{C-CF}_2\text{CF}_3 \]

(6) (5) (4) (3) (2) (1)

b)

c)

\[ \text{CH}_3\text{CO}_2\text{CH}_3 \] \[ \text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3 \] \[ \text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O} \] \[ \text{CH}_3\text{CO}_2\text{C(CH}_3)_3 \]

(1) (2) (3) (4)
Problem 33: Polymers

1. The volume of the Lamax is 40.9 cm x 34.1 cm x 17.0 cm = 23.7 dm³. Consequently, the Lamax will be filled with m = Vd = 23.2 kg.
This quantity corresponds to \((23200/10^6) \times N_A\) Vergina Star Copolymers, or \(0.0232 \times N_A\) Vergina Star Copolymers, where \(N_A\) is the Avogadro number.

2. The following reaction scheme should be followed in order to synthesize the Vergina Star Copolymer:

\[
s-\text{BuLi} + \text{CH}_2=\text{CH} \rightarrow \text{CH}_2=\text{CH} \text{Li}^+\]

\[
\begin{array}{c}
\text{PS} \\
\text{CH}_2=\text{CH} \text{Li}^+ \\
\end{array}
\]

\[
\begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\]

\[
\text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl}
\]

\[
+ 8 \text{LiCl}
\]

Due to the steric hindrance of the styrrillithium anion, only one polymeric chain can react with each \(-\text{SiCl}_2\) group.

\[
(A) + \begin{array}{c}
\text{CH}_3 \\
\text{CH}_2=\text{C}=\text{CH}=\text{CH}_2 \text{Li} \\
\end{array}
\]

25
Due to the lower steric hindrance of the polyisoprenyllithium living ends, the reaction goes to completion.
### Fundamental constants

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Speed of light</td>
<td>c</td>
<td>299 792 458</td>
<td>m s⁻¹</td>
</tr>
<tr>
<td>Permeability of vacuum</td>
<td>µ₀</td>
<td>(4\pi \times 10^{-7} = 12.566\ 370\ 614 \ldots \times 10^{-7})</td>
<td>N A⁻²</td>
</tr>
<tr>
<td>Permittivity of vacuum</td>
<td>ε₀</td>
<td>(1/\mu c^2 = 8.854\ 187\ 817 \times 10^{-12})</td>
<td>C² m⁻² N⁻¹ or F m⁻¹</td>
</tr>
<tr>
<td>Planck constant</td>
<td>h</td>
<td>6.626 068 76 \times 10^{-34}</td>
<td>J s</td>
</tr>
<tr>
<td>Electron charge</td>
<td>e</td>
<td>1.602 176 462 \times 10^{-19}</td>
<td>C</td>
</tr>
<tr>
<td>Electron mass</td>
<td>mₑ</td>
<td>9.109 381 88 \times 10^{-31}</td>
<td>kg</td>
</tr>
<tr>
<td>Proton mass</td>
<td>mₚ</td>
<td>1.672 621 58 \times 10^{-27}</td>
<td>kg</td>
</tr>
<tr>
<td>Avogadro constant</td>
<td>Nₐ</td>
<td>6.022 141 99 \times 10^{23}</td>
<td>mol⁻¹</td>
</tr>
<tr>
<td>Faraday constant</td>
<td>F</td>
<td>96 485.3415</td>
<td>C mol⁻¹</td>
</tr>
<tr>
<td>Boltzmann constant</td>
<td>k</td>
<td>1.380 650 3 \times 10^{-23}</td>
<td>J K⁻¹</td>
</tr>
<tr>
<td>Molar gas constant</td>
<td>R</td>
<td>8.314 472</td>
<td>J K⁻¹ mol⁻¹</td>
</tr>
<tr>
<td>Atomic mass unit</td>
<td>u</td>
<td>1.660 538 73 \times 10^{-27}</td>
<td>kg</td>
</tr>
</tbody>
</table>


The unit 1 M is commonly used as an abbreviation for 1 mol dm⁻³.

1 cal = 4.184 J

The constants listed on this page and the periodic table will be available to students during the 35th ICChO.